Letters to the Editor

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Communications

Detection and Identification of Triplet States of H_2O by Electron Impact

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It has been shown previously[1–4] that the angular behavior of the differential cross section for exciting molecular electronic states by low-energy electron impact is a useful tool in distinguishing transitions which are optically spin forbidden from those which are spin allowed. We have used this method to investigate water vapor and have detected and identified at least two singlet→triplet transitions. One is a broad feature having a maximum intensity at about 4.5 eV excitation energy and the other has a sharp maximum at 9.81 eV. The first one had been detected previously[5–10] and the triplet state character of the upper state involved had been implied.[5] The second one had not previously been detected. We show that the differential cross section for both of these excitation processes have an angular dependence characteristic of singlet→triplet transitions.

We have obtained electron impact spectra of water vapor at impact energies E_0 ranging from 8 to 55 eV and scattering angles θ from 0° to 90°. The experimental apparatus and procedures have been described earlier.[3,4,11,12] The scattering intensities varied linearly with sample pressure under the experimental conditions used (10^{-3} torr as measured with an uncalibrated ion gauge). Figure 1 shows the angular dependence of the scattered signal intensities $[I/I(\tilde{X}\,^1A_1\rightarrow\tilde{A}\,^1B_1)]$ for the excitation of five electronic states relative to the intensity of the $\tilde{X}\,^1A_1\rightarrow\tilde{A}\,^1B_1$ transition. The latter was measured at an excitation energy of 7.5 eV and the instrumental resolution was set at 0.1 eV. The excitation energies for the other transitions are indicated in parentheses. The experimental points were obtained over a period of 2.5 years. From the curves it can be seen that the cross sections for transitions to the $\tilde{A}\,^1B_1$, $\tilde{B}\,^1A_1$, $\tilde{C}\,^1B_1$, and $\tilde{D}\,^1A_1$ states have similar angular dependencies, whereas those corresponding to excitation energies of 4.5 and 9.81 eV show the typical behavior of singlet→triplet excitations.[3,4] There was no indication of the transition at 6.2 eV seen by Skerbele *et al.*[9]

The 4.5 eV feature is weak and quite broad, extending from about 4 eV to 6.5 eV, where it blends into the tail of the $\tilde{A}\,^1B_1$ system. Theoretical calculations performed to date[13–15] do not predict excited electronic states for water with vertical excitation energies from the ground state below 6 eV. From his electron-trap experiments, Schulz implied[5] that the transition could be due to the $\tilde{a}\,^3B_1$ state. The angular behavior we observe has some of the characteristics of a doubly forbidden transition.[1,3] This, together with the broadness of the transition, suggests that a contribution from the $\tilde{b}\,^3A_2$ state cannot be excluded. Reasons for the weakness of the transition, in addition to its spin forbiddeness, may be the smallness of the Franck–

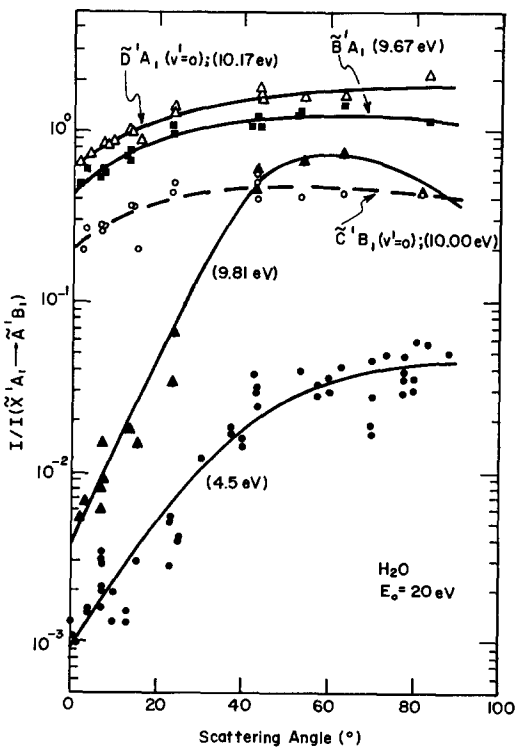

FIG. 1. Intensities of several electronic transitions in water, relative to that of the $\tilde{X}\,^1A_1\rightarrow\tilde{A}\,^1B_1$ transition, as a function of scattering angle. Transition energies are indicated in parentheses. Impact energy: $E_0=20$ eV (not corrected for contact potential). Resolution: 0.10 eV.

Condon factors (the $^3B_1$ state is linear) or the partial double forbiddeness just mentioned, or both. Since the lowest dissociation energy of H_2O (into $O+H_2$) is 5.03 eV, one or both of those states must be attractive by at least 1 eV.

Another confirmation of the singlet→triplet state character of the 4.5-eV transition is the variation of its $I/I(\tilde{X}\,^1A_1 \rightarrow \tilde{A}\,^1B_1)$ intensity ratio with impact energy. This ratio is about 0.1 at threshold[5,8] (electron-trap method), 0.06 and 0.002, respectively, at scattering angles of 10° and 20° and $E_0=20$ eV (this work), and 0.001 at a scattering angle of 5° and $E_0=53$ eV.[9] This behavior is in general agreement with the energy dependence of the cross sections for singlet→triplet and singlet→singlet transitions. The former ones have a maximum slightly above threshold, whereas the latter have in general a broad maximum 50 to 100 eV above threshold.

The 9.81 eV feature has a width of 0.1 eV or less and is superimposed on the broad $\tilde{X}\,^1A_1 \rightarrow B\,^1A_1$ transition. This suggests that the geometry of the corresponding triplet state may be similar to that of the ground state. At low scattering angles the transition intensity is weak compared to the $\tilde{C}$ and $\tilde{D}$ transitions but above about 40° it becomes more intense than the $\tilde{C}$ one. The integral cross section for the 9.81 eV singlet→triplet transition is about 15% of the strong $\tilde{X}\,^1A_1 \rightarrow D\,^1A_1$ ($v'=0$) one and about an order of magnitude larger than the 4.5 eV one. The corresponding triplet states may be of importance in the radiation chemistry of aqueous solutions. Smaller *et al.*[16] have investigated the H atom signal in the pulse radiolysis of such solutions by electron spin resonance. They have observed an effect that can be attributed to a precursor species whose lifetime is of the order of 10 μsec. This species could be one of the triplet states reported above.

A detailed account of these results, as well as differential cross sections for these and other transitions at several impact energies, will be reported later.

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Direct Demonstration of Nonrandomization of Internal Energy in Reacting Molecules. Rate of Intramolecular Energy Relaxation*

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The RRK–RRKM theories[1] predict a random incidence of unimolecular decomposition events following rapid intramolecular relaxation of internal energy. Previously,[2] we described a novel and direct test of the energy randomization postulate that supported earlier evidence concerning the general usefulness of this postulate at the high levels of vibrational excitation that characterize reacting molecules.[3] We have now greatly extended this test in comprehensiveness and have demonstrated in graphic fashion, independently of theoretical constructions, a failure of complete randomization. The total decomposition was separated into a conventional randomized and also a "non-randomized" component; also, a quantitative measure of the over-all rate of intramolecular energy relaxation has been obtained in this case.

We use chemical activation in order to symmetrize

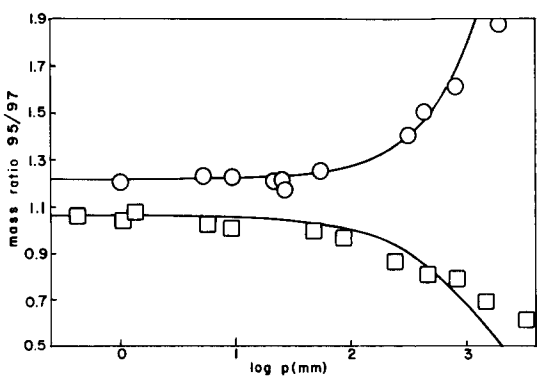

FIG. 1. 95/97 mass ratios for the HVC+CD_2 system, ○, and the HVC-d_2+CH_2 system, □. The solid curves are the fit provided by the values and model in the text.